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A SUBSTITUTE LIQUID FOR AFFF (AQUEOUS FILM FORMING FOAM) CONCENTRATE FOR CHECKING PROPORTIONERS

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The high cost of Aqueous Film Forming Foam (AFFF) concentrate makes it expensive to conduct the routine testing of shipboard High Capacity Fog Foam station proportioners and has created the desire for a lower cost substitute material. The selection of an appropriate liquid to simulate the performance of an AFFF concentrate in a proportioning system is based on matching the viscosity characteristics for pumping and the index of refraction characteristics for analysis.

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Mixtures of glycerin and water were found capable of reproducing these properties of all existing AFFF concentrates when used in strengths of 40 to 87% glycerin. The extra logistics and manipulations required to use a simulated liquid should be considered in making a decision on its use.

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R. L. Gipe, C. S. Butler and H. B. Peterson

BACKGROUND

The routine maintenance procedures for the High Capacity Fog Foam stations aboard aircraft carriers and some systems on other vessels require that a check be made on the operation of the water-motor proportioners. One level of checking can be accomplished by recirculating AFFF concentrate through the proportioner pump and back into the tank; however, the highest level of checking can only be done by actually pumping concentrate into the risers supplying the outlets. A serious drawback to the more frequent checking of the stations has been the high cost of the AFFF concentrate which is necessarily consumed. It has been proposed that a material simulating the characteristics of AFFF concentrate, but available at a lower cost, would be of benefit to the Navy and NRL was requested to recommend a suitable substitute.

INTRODUCTION

From the work done over the past years it has been found that viscosity is one of the more significant properties of the liquid being handled in the positive displacement pump portion of the proportioner. The high pressure existing on the discharge side of the pump forces liquid back through the axial and radial clearances in the pump to the low pressure existing at the intake side. The more viscous the liquid, the less the volume of liquid passing through these narrow openings.

The objective was thus to find a method of duplicating AFFF concentrate viscosity at a reasonable cost. It was also judged to be of importance to have a material with a suitable refractive

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index range so that the solutions could be analyzed by the same hand refractometer presently used for AFFF solutions.

High molecular weight polymers of ethylene oxide and carboxymethylcellulose are dry materials which, added to water in small amounts, will increase its viscosity sufficiently, but both were judged to be too difficult to handle and put into solution. Glycerin, a readily available liquid material, was also tested for use in this investigation and was found to give the desired performance. Because of its low cost, ready availability and appropriate refractive index, other potential agents were not investigated.

EXPERIMENTAL RESULTS

The first AFFF concentrate fully compatible with sea water and used in shipboard systems was designated FC-195. This formulation has been followed by others known as FC-196, FC-199, and FC-200. A considerable drop in concentrate viscosity occurred in those materials subsequent to FC-195. The viscosity-temperature characteristics of each of these concentrates are given in Figure 1. Data are also given for protein foam liquid, for which the proportioning equipment was originally designed, for FC-200 Lot 3002, an experimental concentrate made to have a viscosity comparable to protein foam liquid, and for FC-194, an earlier fresh water compatible material.

All the viscosity measurements reported in this work were determined with a capillary viscometer of the appropriate size and in accordance with ASTM D445-65.

Figure 2 is a plot of the viscosities of mixtures of water and glycerin and shows the range of viscosities that can be achieved with this system at 77°F.

A comparison was made between the temperature-viscosity characteristics of a water-glycerin mixture and an AFFF concentrate. These data are given in Figure 3.

Finally, a series of runs was conducted on a FP-1000 proportioner comparing actual AFFF concentrates and glycerin-water mixtures of similar viscosities in order to detect the existence of any non-viscosity related phenomena. (The viscosities of the liquids were selected in part to check the characteristics of the

proportioner over a small range of concentrate viscosities.) Five liquids were employed: (1) water with a viscosity of 1 centistoke (CS), (2) an AFFF concentrate diluted with water to give 3 CS, (3) a glycerin-water mixture of 3 CS viscosity, (4) a mixture of AFFF concentrates to give 6 CS, and (5) a glycerin-water mixture of 6 CS viscosity. These results are summarized in Figure 4.

Refractive index measurements were made of the water-glycerin mixtures to see if the optical properties of the solutions were sufficient to provide a workable range on the hand refractometer now used on shipboard for AFFF solution analysis. In Figure 5 are plotted a concentration-refractive index relationship for an AFFF concentrate and a corresponding curve for a simulated concentrate made up of glycerin and water. The glycerin-water mixture selected was of such a ratio as to create a 3 CS viscosity concentrate. This meant that the glycerin content was very low and would represent the lowest amount which would ever be used in a simulated concentrate.

DISCUSSION

Performance of Glycerin-Water Mixtures

From the data of Figure 1 it can be observed that there have been considerable changes in the viscosity of AFFF concentrates over the years of their development. None of them has been very close to the characteristics of protein foam liquid for which most of the fire fighting equipment in the Navy was designed. In those systems where the concentrate proportioning is viscosity dependent, the delivered concentrations will have been affected accordingly. In many cases the "reserve strength", or safety factor, inherent in the concentrate composition has meant there has been little compromise in fire suppression capability with either lean or rich solutions. However, in some extreme cases it could have meant the complete lack of concentrate introduction. An earlier report (1) has covered this subject in detail.

The characteristics of Lot 3002 indicate that it is not a problem to reproduce a viscosity comparable to protein foam with an AFFF concentrate. The most probable explanation for why it has not been done earlier has been the lack of appreciation of the shipboard proportioning requirements and the limited amount of concentrate used on shipboard, as compared to other consumers.

The range of viscosities, Figure 2, which may be obtained by mixtures of glycerin and water varies from 1 CS for pure water to approximately 900 CS for pure glycerin at 77°F. This range easily encompasses the viscosities of all of the concentrates covered in Figure 1 and at all temperatures between 32° and 120°F. Thus, glycerin-water mixtures have no limitations in this area and the curve in Figure 2 will enable selection of the proper proportions to simulate any AFFF or protein concentrate.

The effect of temperature change on the viscosity of a glycerin-water mixture is given in Figure 3 and is compared to an AFFF concentrate of approximately the same viscosity. This was done in order to determine if an error would be introduced if a glycerin-water mixture was selected to match an AFFF concentrate at 77°F but then actually used at a different temperature. Examination of the two functions show that they are not precisely parallel, indicating their temperature characteristics are not identical. However, it is believed that no appreciable error would be introduced. A glycerin-water combination prepared to the same viscosity as FC-199 at 80°F would have close to the same viscosity as FC-199 if both were taken at 40°, or to 100°F, and any results obtained with glycerin-water should be acceptable.

Figure 4 gives the actual FP-1000 water-motor proportioner performance comparison between AFFF concentrate and a glycerin-water simulated concentrate at two viscosities, 3 and 6 CS. Although there was some difference noted between the two liquids at 3CS, there was essentially no difference at 6 CS and it is believed that the glycerin-water mixtures may be taken as fully acceptable substitutes for the concentrates. It may also be seen from these data that the solution concentrations were noticeably affected by even slight changes in the viscosity of the material being pumped.

During the period of testing when AFFF concentrate was being recirculated as a conservation practice, the viscosity was checked regularly in order to ascertain whether the shearing action of the pump was affecting a breakdown of any polymers in the fluid which might influence the viscosity. No evidence of shear degradation was detected.

The data in Figure 5 show the relationships of concentration and refractive indices for glycerin-water and AFFF solutions. The results for AFFF are similar to the calibration curves prepared on shipboard preparatory to making an operational check of a system. Normally such a calibration curve is made up for each station as it is checked because the different concentrates produce different slopes, and sea water contamination, if present, will shift the curve downward and introduce errors in the final analyses. The glycerin-water mixture shown in Figure 5 was chosen to simulate a 3 CS concentrate. Because the glycerin-water mixture curve and the AFFF curve both fall well within the range of the hand refractometers now in use, no analytical problem would be encountered by the use of glycerin-water mixtures as a substitute concentrate. On the contrary, the increased steepness noted in the glycerin-water mixture will improve the accuracy of determinations over the AFFF concentrates.

Estimated Cost

The glycerin used in the study was made by Shell Chemical Co., 99.5% purity, and cost $0.29 per pound, or $3.05 per gallon, purchased in a small quantity from Baltimore Chemical. This cost per gallon probably represents the highest possible for this grade, and purchase in commercial quantities would reduce the price to approximately $0.24 per pound.

The cost per gallon of simulated AFFF concentrate will, of course, depend on the viscosity of the specific concentrate to be simulated. Table I presents the estimated costs of the glycerin (based on the NRL cost) required to make up one gallon of simulated concentrate. The balance of the mixture is water.

Table I

Glycerin Costs for Simulated AFFF Concentrates

Concentrate	Glycerin Content %	Glycerin Cost Per Gallon Mix	Viscosity 80°F Centistokes
FC-195	87	$2.70	110.
FC-196	50	1.52	6.1
FC-199	48	1.47	5.9
FC-200	40	1.22	4.2
Protein	70	2.14	20.

With the current costs of FC-200 running about $5 per gallon, it may be seen that the simulated version of FC-200 would cost about one quarter that of the real material.

Operational Considerations

Although the substitution of a glycerin-water mixture would reduce the cost of material consumed in running a proportioner check, the operational considerations must also be taken into account.

Emptying of the 600-gal. storage tanks, replacing with a simulated concentrate, running a check, and then putting the original concentrate back into the tank would appear to be an almost prohibitive procedure. The alternative would be to install a tee fitting in the proportioner suction line downstream of the Powertrol valve which would permit connecting a 50-gallon tank of simulated material brought to the station for the purpose. In addition to the costs of modifying the piping arrangement at each station, new possibilities for errors will be introduced and reliability will be compromised.

A test procedure would have to be worked out around the objective of the test. If the objective was to ascertain what a particular proportioning station would do under operational conditions, the viscosity of the contents of the tank would have to be determined and the simulated concentrate prepared accordingly for that station. This would be a fairly sophisticated operation for shipboard personnel to conduct. Tanks on aircraft carriers have been found to contain materials ranging in viscosity from 4 CS to 100 CS. If the objective was to ascertain the relative operating condition of a proportioner, a standard mix of simulated concentrate could be used for all stations.

By the use of appropriate tables, data obtained with a 6 CS simulated concentrate could be translated into what the solution strength would have been for the actual viscosity of the concentrate in the tank. Also, the minimum acceptable limit for proportioner performance could be established on the basis of a certain fixed viscosity. For example, every proportioner to be classed as acceptable would have to achieve an output solution strength of at least 4.5% when using a test concentrate of 6 CS at a stipulated flow rate. (In those cases where the tank contents were of a higher than 6 CS viscosity, higher percentages would be required

at the low end of the flow scale in order for the unit to be considered acceptable.

Environmental Impact

The possibility of conducting proportioner tests while the ship is in port raises questions as to the environmental considerations involved. These might be different from those when testing at sea.

The Director of the Advisory Center on Toxicology of the National Research Council/National Academy of Sciences has stated (2) that solutions of glycerin in water are biodegradable in the sea. The 3M Co. has also stated that its AFFF product is biodegradable and will have no adverse effects on the environment (3). The above statements would indicate that either product could be used at sea or in port without creating a problem, however, such might not be the case. Under the strictest interpretations, practically anything undrinkable by humans is unfit to discharge over the side into the sea or into an estuary. Whether a concentrate, or substitute concentrate, is simply biodegradable may not be adequate justification for its use.

Certainly visibility of any discharge over the side is an important aspect and a large raft of snow-white AFFF floating in a harbor is definitely an attention-getter. Aeration of a glycerin-water mixture does produce a froth but it is less stable than AFFF. From this standpoint, perhaps either material might be unacceptable for in-port discharge. In the event the visibility problem does become the critical one, other test techniques could be worked out whereby a non-aerated discharge could be run through a closed hose system over the side, but terminating below the water surface or into a shore sanitary system.

Other Methods

After the above work with glycerin had been completed, the 3M Company reported on some similar work they had done using polyvinyl alcohol as a thickening agent. They prepared a concentrate with a duPont product, Elvanol 71-30, in a 35% ethylene glycol-water mixture. Further dilution in water gave liquids of 6, 15, and 30 CS viscosity with 1, 2, and 3% respectively of Elvanol. The ethylene glycol was added in order to provide for concentration analysis by means of the refractometer. According

to 3M this is also a suitable substitute.

3M also prepared a concentrate of high viscosity, 9000 CS, which could be used to increase the viscosity of FC-196, FC-199, and FC-200 already in shipboard tanks without decreasing their fire performance capability. Typically, adding 10% by volume would raise the viscosity from 4 to 20 CS.

Such an approach could be taken to prepare a simulated concentrate from water on shipboard. (It would not be necessary, however, to add the fluorocarbon components.) Slightly over 15% of this concentrate would be required to increase the viscosity of water from one to 20 CS. However, effort is required to dissolve this concentrate uniformly in water.

The 3M Company is presently giving consideration to the marketing of such a product specifically for the testing of fire suppression systems. Apparently there has also been an expression of interest from the owners of industrial installations. No information is available as to a proposed cost of the material.

CONCLUSIONS

It is feasible to simulate AFFF concentrates for proportioner testing by adding appropriate agents to water to give it the proper viscosity and refractive index.

The cost of simulated concentrates will depend in part on which AFFF concentrate it is desired to simulate because their viscosities vary. The cost will also depend on whether it is procured as a ready-to-use mixture or whether the final preparation and mixing is done on-site from a highly concentrated liquid. However, the final costs could be on the order of half the present cost of real AFFF concentrate.

NRL has found glycerin-water mixtures to be suited for the purpose and the 3M Company has found polyvinyl alcohol-ethylene glycol-water mixtures to be suitable also.

RECOMMENDATIONS

The use of simulated concentrates for proportioner testing on shipboard is not recommended unless no other recourse is available. It is believed that the logistical problem of having a simulated concentrate in the supply system, the operation of change-over from real concentrate to simulant and then back to real concentrate for each test, and the increased potential for introducing errors and confusion would not be justified on the basis of the differential costs per gallon of the simulated and real concentrates.

In the event that it is decided for ecological reasons to proceed with the use of a simulated concentrate in spite of the cited problems, it is recommended that commercial sources be approached as potential suppliers of a simulated AFFF concentrate based on a glycerin-water mixture or a polyvinyl alcohol-ethylene glycol-water mixture.

REFERENCES

1. Gipe, R. L. and Peterson, H. B., "Proportioning Characteristics of Aqueous Film-Forming Foam Concentrates", NRL Report 7437, 20 July 1972.

2. Private communication to Dr. Homer W. Carhart, NRL August 1973.

3. 3M Company ltr to NAVMAT dated 29 Feb. 72.

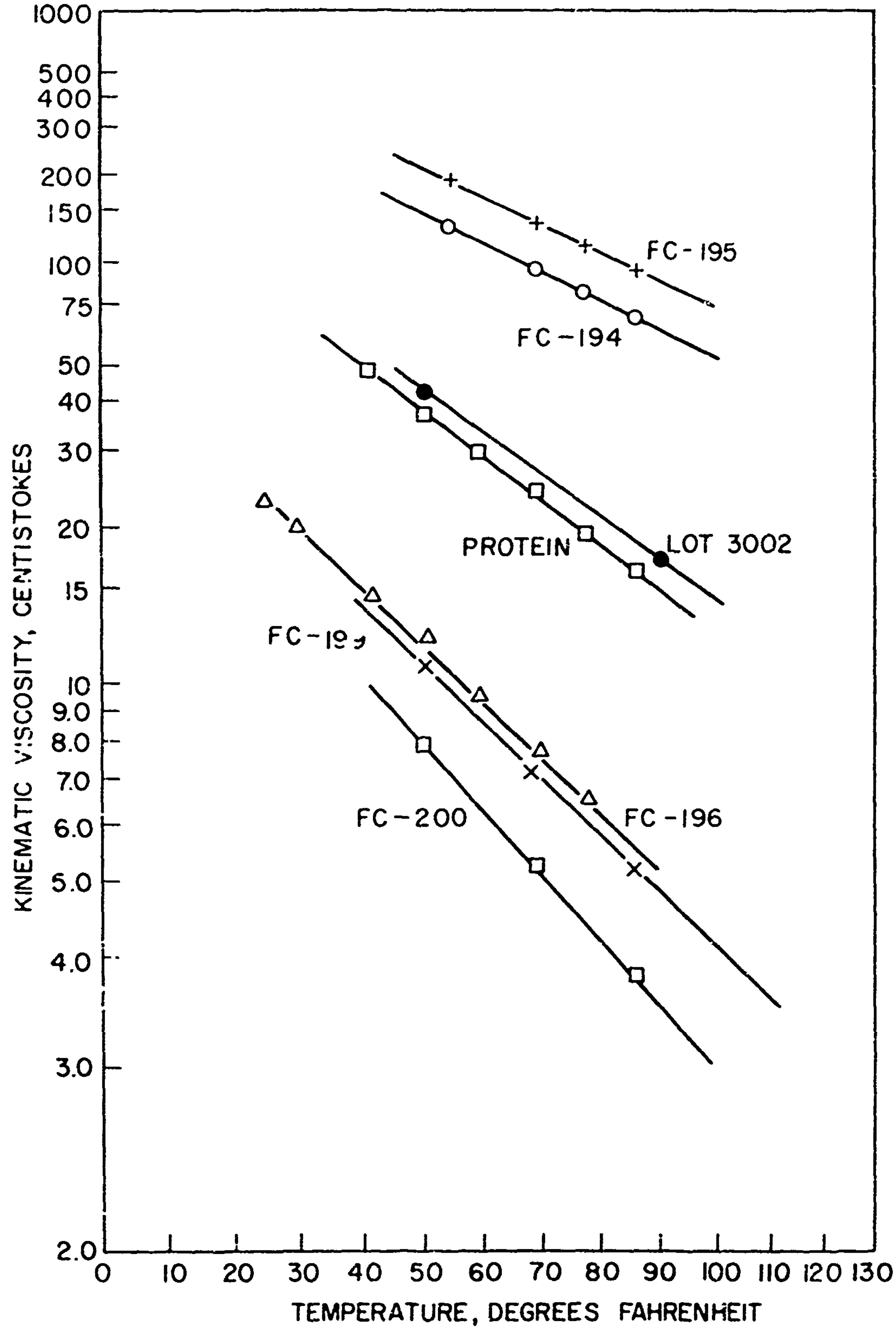

Fig. 1 - Viscositv of AFFF concentrates as a function of temperature.

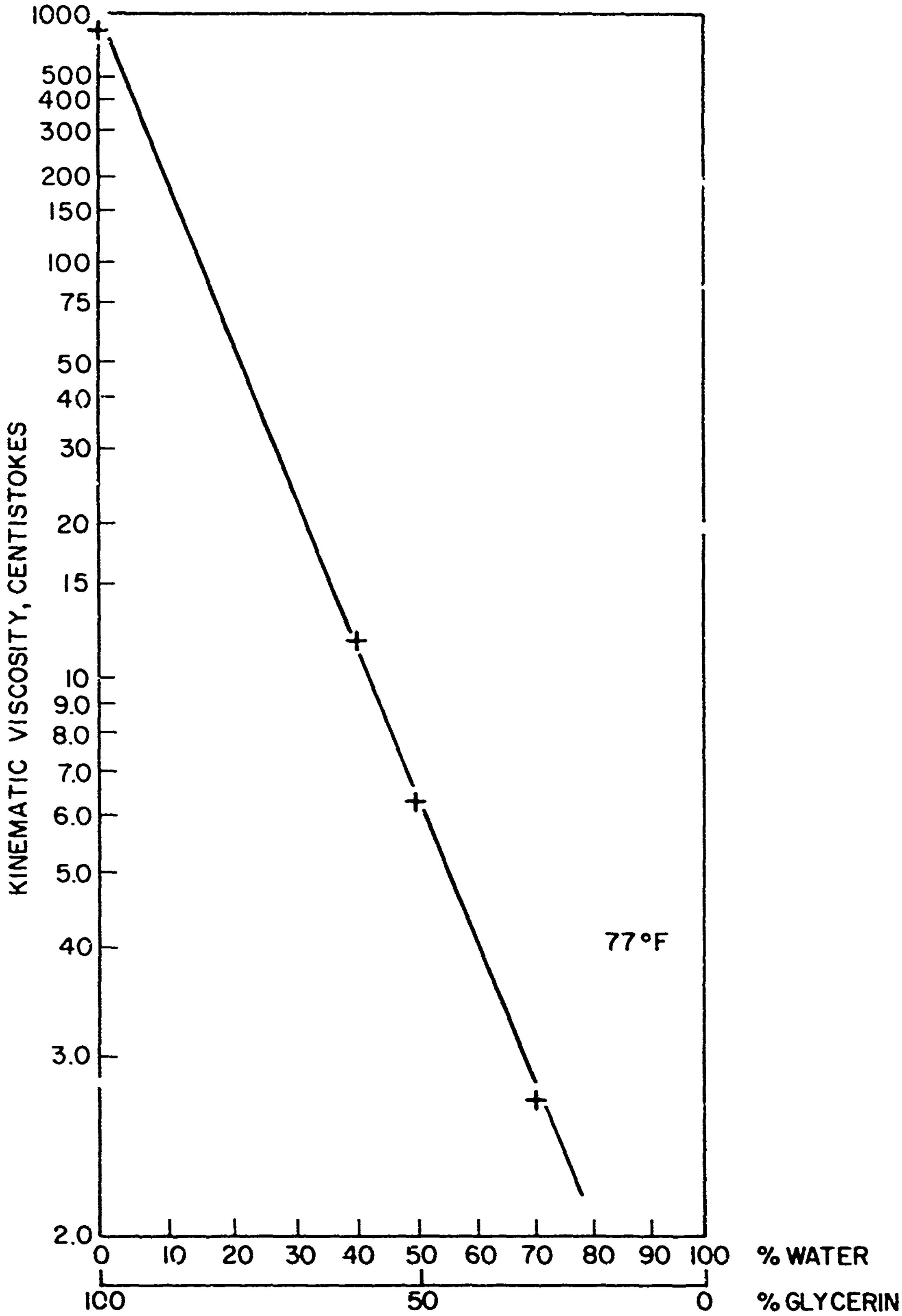

Fig. 2 - Viscosity of glycerin-water mixtures.

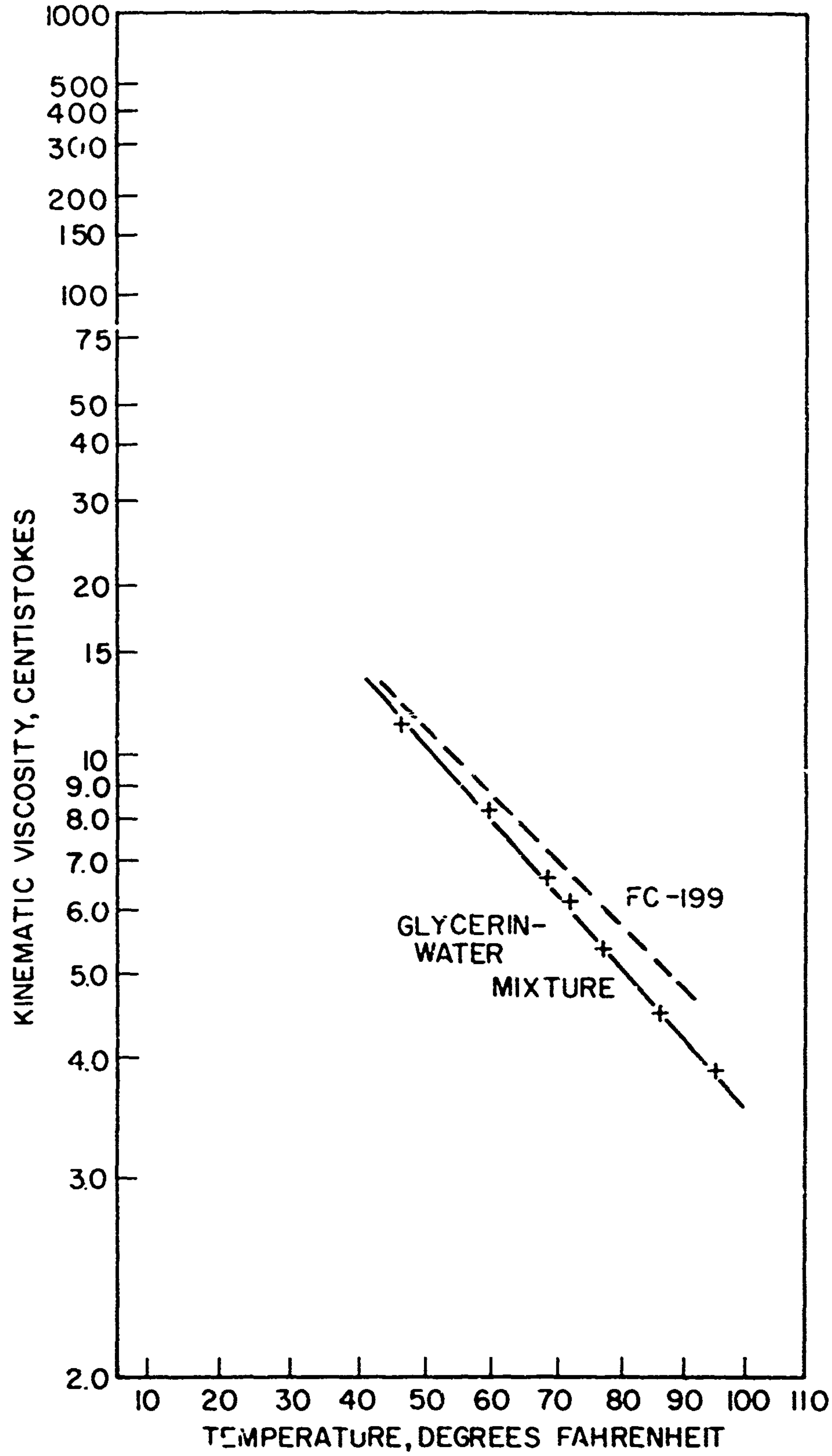

Fig. 3 - Viscosity-temperature relationships of an AFFF concentrate and a glycerin-water mixture.

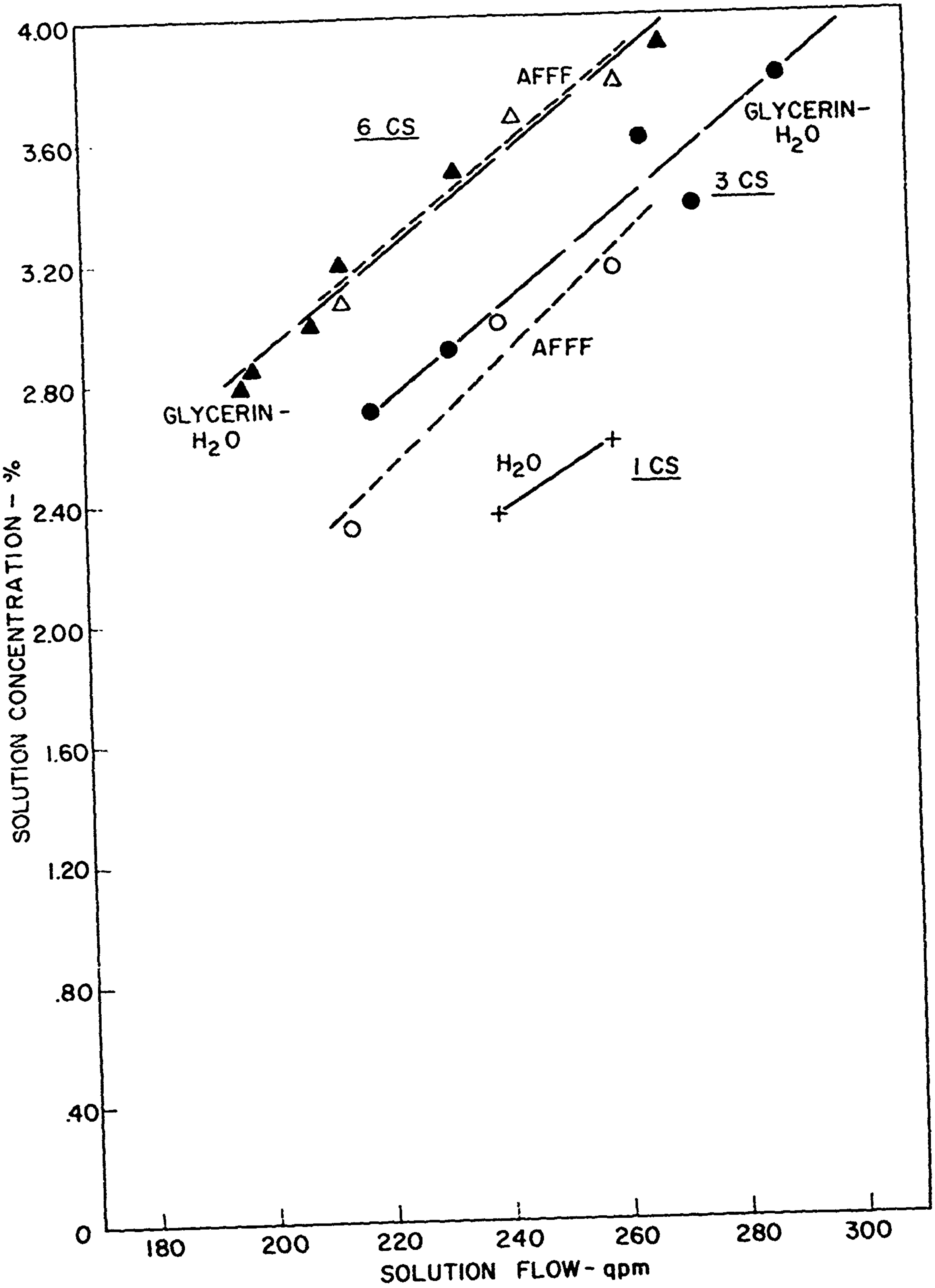

Fig. 4 - Comparative performance of AFFF concentrates and glycerin-water simulated concentrates in an FP-1000 proportioner.

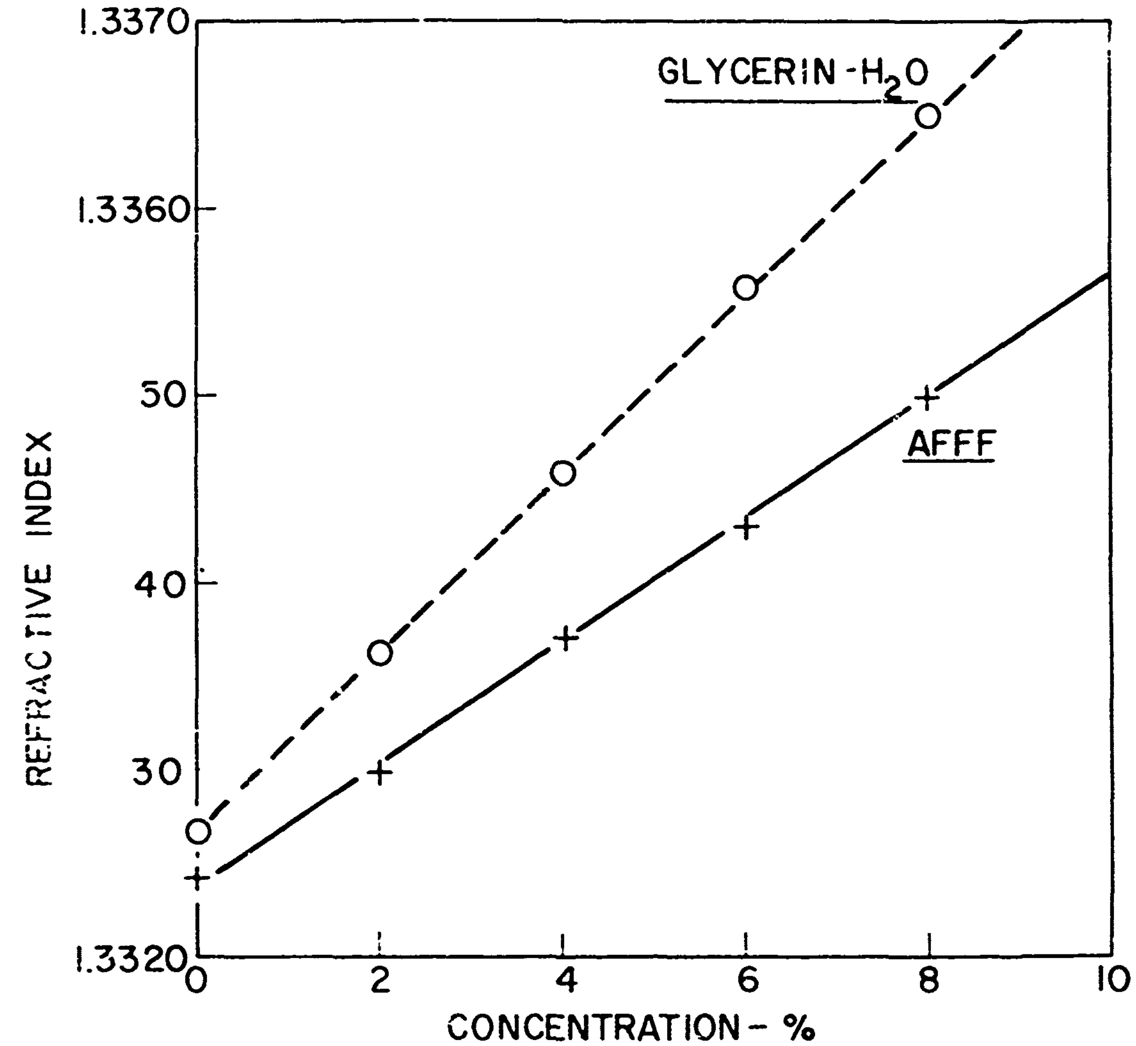

Fig. 5 - Refractive index of solutions prepared from an AFFF concentrate and a simulated concentrate of glycerin and water.